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ORIGINAL ARTICLE

Biomass characterization of wild and cultivated cardoon accessions and estimation of potential biofuels production

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Abstract
Cardoon is considered an interesting raw material to obtain second-generation biofuels, due to its perennial culture condition and its rare use as food. In addition, cardoon, being a rustic species, requires few inputs and has fast growth and high lignocellulosic biomass production. However, despite its large genetic variability worldwide, both cardoon botanical varieties were subject only to few (cultivated cardoon)/zero (wild cardoon) breeding programs. The aims of this study were (I) to characterize biomass quality and quantity of genotypes of wild and cultivated cardoon in order to produce different types of biofuels and (II) to identify the most promising accessions to be included in breeding programs for bioenergy characteristics or to be incorporated in the local agro-productive system. The performance of twelve *Cynara cardunculus* L. accessions (six cultivated cardoons and six wild cardoons) was compared through biometric, chemical, and energetic characteristics. Moreover, the potential bioethanol and biomethane yields and the energy potentially generated from direct combustion were calculated for each botanical variety. Significant differences were found between botanical varieties for several biometric traits, but not in chemical traits except for ash content. Results indicate that cardoon biomass, especially cultivated cardoon, has characteristics that make this species a promising candidate to be grown for energy purposes under very low crop inputs in the local edapho-climatic conditions. In addition, our screening identified an accession that stands out based on yield, biomass composition, and potential to produce different types of biofuels/bioenergy.

Keywords *Cynara cardunculus* · Bioenergy · Biomass · Genetic variability

1 Introduction

In the last decades, environmental degradation and climate change have reached a high relevance worldwide. The need for a new energetic model based on renewable sources has caught the attention of the scientific community. In this sense, there is an increasing interest in alternative uses of agro-industrial residues and new crops for energy applications.

Biomass is a "clean" energy feedstock obtained from organic matter by biological processes. It is a renewable energy source that can provide, in the short-term,

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alternative fuels such as bioethanol, biodiesel, or biogas [1, 2]. Lignocellulose is the most abundant renewable biomass with an annual production estimated at 150 billion of Mg worldwide [3].

Energy crops that are perennial, non-food, and non-competitive with food crops for lands are considered the future of the bioenergy industry. Compared with crops used to obtain first-generation biofuels, these species have faster growth, require fewer inputs, produce more energy, and reduce greenhouse gas emissions as compared to annual cropping systems [4]. These species are also characterized by high biomass yield and high rusticity, given by characteristics such as drought and disease resistance, vigor, growth earliness, regrowth ability, and adaptation to marginal areas and poor soils, in parts due to its mechanism of resistance to environmental stress [5–7].

Cynara cardunculus L. is a species complex that includes globe artichoke [var. *scolymus* (L.) Fiori], cultivated cardoon (var. *altilis* DC.), and the wild cardoon [var. *sylvestris* (Lamk) Fiori], together with other six wild species [8]. Due to its relatively low crop inputs, large dry biomass productivity, low moisture content, and high calorific value, cardoons have gained relevance among energy crops expanding in semi-arid regions [9]. This species is a perennial herb which offers a wide spectrum of biomass uses for different industrial applications, among which the most promising seems to be bioenergy production [10]. As a member of the Asteraceae family, like sunflower and safflower, cardoon achenes accumulate oil in the endosperm. The suitability of this oil for biodiesel production has been studied extensively [11–16]. The use of extraction protein panels obtained after oil extraction as a natural by-product for pigs feeding has also been reported [17]. After the mature flower heads are cut off for seed collection, the remaining lignocellulosic biomass can be collected and destined for bioenergy production.

These botanical varieties were subject only to few (cultivated cardoon)/zero (wild cardoon) breeding programs. Nevertheless, several authors reported high genetic variability, both between and within botanical varieties, for many traits including biomass production [18–24]. The inclusion of a new crop with a specific purpose into an agricultural system requires uniformity between plants for productive traits and high agronomic performance (adaptation with high productivity and good quality) in the culture area. For this reason, the aims of this study were (1) to characterize quantitative and qualitative traits associated to energy production in wild and cultivated cardoons biomass growing under local edapho-climatic conditions and (2) to identify the most promising accessions to be included in breeding programs for bioenergy characteristics or to be incorporated in the local agro-productive system.

2 Materials and methods

2.1 Plant material, local climate, soil, and crop management

Twelve *C. cardunculus* L. accessions (six cultivated cardoons and six wild cardoons) were compared in a randomized experimental design with three replications of 20 plants. The planting frame was 0.90 m between rows and 0.75 m between plants in the rows, achieving a density of about 15,000 plants ha^{-1}.

Among cultivated cardoons, three accessions were traditional Spanish varieties ('Lumbier', 'Blanco Peralta', and 'Lleno de España'), whereas the other three were varieties belonging to local farmers and were named Farmer 1, Farmer 2, and Farmer 3. Wild accessions were ecotypes collected in verge and/or wild (non-cultivated) areas of different regions of Argentina and Uruguay and named according to their origin sites (Table 1).

Both the wild accessions and those called Farmer 1, 2, and 3 were collected as achenes at the end of the productive cycle. To ensure the purity of the collected accession, the non-existence of *C. cardunculus* plants (neither wild nor cultivated) in at least 500 m around was verified. Therefore, this trial was initiated by achenes for all accessions, which were implanted at the Rosario National University experimental field, located in Zavalla City, Santa Fe province, Argentina (33° 01′S; 60°53′W). This region is characterized by a temperate climate and loamy soil. The soil characteristics are as follows: pH (7.6), organic matter (2.9 %), nitrate (23.96 ppm), assimilable phosphorus (32.73 ppm), and exchangeable potassium (2.1 meq/100 g). Zavalla belongs to the semi-monsoon rainfall pattern; rainfall varies between 678 and 1338 mm with an average of 990 mm. The average temperature is 17 °C. The average frost-free period comprises from early September to early June, resulting in a frost-free period of 275 days [25, 26]. During the test year (2019), rainfall was 10% below the average, and the distribution by quarters was as follows: 210 mm in the first, 180 mm in the second, 220 mm in the third, and 270 in the fourth quarters.

Achenes were sown in multi-pot trays, and during the autumn of 2017, at the 4 true leaves stage, plantlets were transplanted at the field. Only nitrogen fertilization (50 kg ha^{-1}) was applied after the autumn re-growth in 2018 and 2019. No pesticide application was required to control pests and pathogens. Weeds were mechanically controlled.

2.2 Biometric evaluation

The trial was evaluated in the second year of growing, when plants completed their full growth. At the maximum

Table 1 Accessions and origins. Geographic coordinates of the wild cardoon accessions collection sites are also cited

Name	Origin
Cultivated cardoon (*Cynara cardunculus* var. *altilis*)	
'Lumbier'	Spanish commercial variety
'Blanco Peralta'	Spanish commercial variety
'Lleno de España'	Spanish commercial variety
Farmer 1	Local variety
Farmer 2	Local variety
Farmer 3	Local variety
Wild cardoon (*Cynara cardunculus* var. *sylvestris*)	
Pergamino	Pergamino, Buenos Aires, Argentina (33° 53′ 22″ S, 60° 34′ 11″ W)
Campana	Campana, Buenos Aires, Argentina (34°10′ 00″S, 58° 55′ 00″ W)
Campi	Campichuelo, Corrientes, Argentina (27° 28′ 16″ S, 58° 50′ 25″ W)
Entre Ríos	Entre Ríos, Argentina (32° 02′ 52″ S, 60° 16′ 52″ W)
Paysandú	Paysandú, Uruguay (32° 19′ 17″ S, 58° 4′ 32.02″ W)
Montevideo	Montevideo, Uruguay (34° 52′ 60″ S, 56° 10′ 0″ W)

vegetative development (October 2019), the following traits were evaluated (without cutting plants) on ten randomly chosen plants per plot: plant height (PH), measured from the plant base to the first head top; plant diameter (PD), measured end-to-end between the two most developing opposite leaves; leaf width (LW) and leaf length (LL), registered on one of the more developed leaves. At the senescent state (February 2020), the heads were manually cut off and reserved for the achenes extraction. Immediately after that, in a second round, all the residual senescent biomass was harvested and weighted. The average weight of ten plants was multiplied by 15,000 to obtain the total yield per hectare (Y) for each variety. Senescent dry biomass samples (2000 g plot^{-1}) were collected respecting the proportion between stems and leaves (70% stems and 30% leaves as suggested by Neri et al [27]). For each sample, a 500 g subsample was dried in a stove at 65 ± 5 °C until constant weight to determine the moisture content (MC) according to the following equation.

$$\mathrm{MC\%} = \left[(\mathrm{ww} - \mathrm{dw})/\mathrm{ww}\right] \times 100$$

where ww is wet weight and dw is dry weight.

2.3 Chemical and energetic evaluation

The rest of the lignocellulosic material collected from each accession (1500 g per accession) was processed in the laboratory, where they were dried, ground, and sieved with a 1-mm mesh before analysis. Ash content, nitrogen (N), and ethereal extract (EE) were determined following the AOAC methods [28]. Volatile solids (VS) were determined by the difference between dry matter (once moisture content has been subtracted) and ash content.

Structural carbohydrate content of the harvested biomass was calculated in terms of dry weight percentage. The lignin content was determined as acid detergent lignin (ADL), cellulose content as the difference between acid detergent fiber (ADF) and ADL, and hemicellulose content as the difference between neutral detergent fiber (NDF) and ADF [29]. Heating values (HV) were determined, on dry basis, by a combustion reaction with high oxygen pressure in an adiabatic bomb calorimeter (UNE 164001 EX). The obtained results correspond to the $\mathrm{HHV_{db}}$ (high heating values). All determinations were made in triplicate.

2.4 Statistical analysis

Normality was assessed according to the Shapiro-Wilk test, and those variables that did not show a normal distribution were transformed by $\sqrt{x}$. The normality of residuals and homogeneity of variances were tested by means of Bartlett's test. Subsequently, the data were subjected to a one-way analysis of variance (ANOVA) using the model:

$$\mathrm{Xi} = \mu + g_{\mathrm{i}} + \mathrm{e}$$

where μ is the experimental mean, g_i is the variety effect, and e is the experimental error.

The mean values were compared by Duncan's multiple range test. All the statistical analyses were performed using the Infogen software [30].

2.5 Potential biofuel/bioenergy yield estimation

Maximum theoretical bioethanol yield (MTY) per Mg of dry matter was calculated according to the following equation [31]:

$$\mathrm{MTY} = [(\mathrm{C6} * 1.111) + (\mathrm{C5} * 1.136)] * 0.511$$

where C6 are sugar polymers main constituent of cellulose and C5 are sugar polymers main constituent of hemicellulose [32].

Bioconversion efficiency of C5 and C6 sugars to ethanol was estimated as 86% and 76%, respectively, as suggested by Shatalov and Pereira [33] for cardoon biomass after being subjected to a selective hydrolysis process.

Theoretical methane yield (B0) was calculated for each accession following the models 1 and 3 proposed by Gunaseelan [34].

Model 1:

$$\mathrm{B0} = 0.35 + 0.38\,C - 1.11\,L + 0.15\,\mathrm{L/ADF} - 0.49\,N - 3.17\,A$$

Model 3:

$$\mathrm{B0} = 0.45 + 0.35\,C - 0.32\,\mathrm{ADF} - 0.18\,L/\mathrm{ADF} - 0.41\,N - 3.40\,A$$

where B0 is the amount of methane ($m^3\ kg^{-1}$ VS); C is the total carbohydrate (cellulose + hemicellulose) (g); L is the total lignin (g); ADF is the acid detergent fiber (g); N is the nitrogen (g); A is the ash (g).

The total thermal energy potentially generated from direct combustion of lignocellulosic biomass was determined as follow [35]:

$$E_{\mathrm{total}} = B_{\mathrm{prod}} * \mathrm{HHV}_{\mathrm{db}}$$

where E_{total} is the thermal total energy (MJ), B_{prod} is the amount of produced biomass (kg), and $\mathrm{HHV}_{\mathrm{db}}$ is the high heating value on dry base.

3 Results

The ANOVA performed for biometric traits (data obtained in October 2019) showed that cultivated cardoons were significantly superior to wild cardoons for plant height, leaf width, and yield (Table 2). When accessions were compared, variability between and within botanical varieties was observed for most traits. The highest values were observed among cultivated cardoon accessions, standing out Farmer 1 and Farmer 2 for plant height (187 and 184 cm, respectively), Farmer 2 and 'Lumbier' for yield (14.22 and 12.80 Mg ha^{-1}, respectively), and 'Blanco Peralta' for plant diameter (208 cm), leaf width (61 cm), and leaf length (120 cm). The lowest values for plant diameter (133 and 151 cm) and leaf length (63 and 62 cm) were also observed among cultivated cardoons (Farmer 1 and 'Lumbier', respectively), whereas wild accessions showed the lowest values for plant height (Pergamino, 103 cm and Campi, 108 cm) and yield (Campi, 3.67 Mg ha^{-1} and Campana, 4.53 Mg ha^{-1}). For leaf width, the cultivated cardoon 'Blanco Peralta' was the only one which differed (with the highest values) from all other accessions.

Lignocellulosic material moisture percentage at harvest time (February 2020) ranged between 2.2 (Entre Ríos) and 9 % (Campana). No significant differences between botanical varieties were found for this trait.

The ANOVA performed for traits related to lignocellulosic material composition showed significant differences between botanical varieties only for ash content where greater values were observed for cultivated cardoons. However, all traits showed significant differences between accessions (Table 2). Farmer 2 showed the highest percentages of hemicellulose, cellulose, and lignin (23%, 48%, and 13 %, respectively). As it is expected for lignocellulosic materials, the EE% were low, ranging from 0.6 (Farmer 2) to 3.00% (Montevideo). Regarding the nitrogen content, Montevideo and Campana (both wild cardoons) represented the extremes of the distribution, with values of 1.24% and 0.38%, respectively. Finally, for ash content, minimum (5%) and maximum (9%) values were attained in cultivated cardoons (Farmer 2 and 'Blanco Peralta', respectively).

The high heating value (HHVdb) did not show significant differences between botanical varieties although significant differences between accessions were found, where both the highest (18.2 MJ kg^{-1}) and the lowest values (17 MJ kg^{-1}) were observed among wild cardoon accessions (Pergamino and Campana, respectively). The maximum theoretical bioethanol yield per hectare was calculated for about 3.30 and 1.50 l ha^{-1} for cultivated and wild cardoon, respectively (Table 3), considering 11.5 and 5 Mg ha^{-1} of biomass production, and 76% of cellulose and 86% of hemicellulose hydrolysis efficiency [31]. The highest values were estimated for the cultivated accessions Farmer 2 (4.55 l ha^{-1}) and 'Lumbier' (3.73 l ha^{-1}).

The theoretical biomethane yield calculated with the model 1 was higher than the one obtained with model 3, reaching values of 2522 $m^3\ ha^{-1}$ and 1790 $m^3\ ha^{-1}$ for cultivated cardoons (models 1 and 3, respectively) and 1300 $m^3\ ha^{-1}$ and 984 $m^3\ ha^{-1}$ for wild cardoons (Table 3). However, regardless of the model used, cultivated cardoon yield was more than double that observed in wild cardoons. The accession Farmer 2 stood out for producing twice as much biomethane than the average production estimated for cultivated cardoons.

The amount of energy potentially generated by direct combustion of the biomass ranged from 66,000 to 251,000 MJ ha^{-1} (Campi and Farmer 2, respectively), and it was 2.3 times higher in cultivated cardoons than in wild cardoons (Table 3). Considering 3.6 MJ is equivalent to 1 thermal kW h, the amount of thermal energy feasible to be generated from the biomass harvested in 1 ha of cultivated and wild cardoons would be, on average, 55,855 thermal kW h and 24,500 thermal kW h, respectively.

Table 2 Biometric traits and chemical composition of aboveground lignocellulosic (leaves and stalks) cultivated and wild cardoons biomass

	Biometric traits**						VS (Mg ha^{-1})	Chemical composition (%)***						HHVdb (MJ kg^{-1})
Accession	PH (cm)	PD (cm)	LW (cm)	LL (cm)	Y (Mg ha^{-1})	MC%		HC	Cel	Lig	EE	N	Ash	
CC	**156.67***	**174.89**	**45.00***	**88.72**	**11.51**	**6.61**	**9.95**	**20.09**	**44.00**	**10.50**	**1.82**	**0.91**	**7.48***	**17.47**
'Lumbier'	130.00^{abc}	151.00^{abc}	42.67^{a}	61.67^{a}	12.80	8.70^{fg}	10.73	20.09^{c}	44.29^{de}	9.89^{ab}	1.81^{bc}	0.77^{bc}	8.20^{ef}	17.12^{c}
Farmer 1	187.33^{d}	132.67^{a}	35.33^{a}	63.33^{ab}	10.54	7.42^{e}	9.08	20.73^{d}	43.77^{cd}	9.83^{ab}	2.25^{cd}	1.09^{efg}	6.96^{cd}	17.71^{i}
Farmer 2	183.67^{d}	176.33^{cde}	45.67^{a}	98.00^{d}	14.22	7.67^{e}	12.46	22.73^{g}	47.93^{i}	12.62^{g}	0.59^{a}	0.50^{a}	5.08^{a}	17.63^{h}
'B. Peralta'	148.00^{c}	207.67^{e}	60.67^{b}	119.67^{e}	10.11	4.60^{bc}	8.76	18.90^{b}	43.18^{bc}	9.63^{a}	1.73^{bc}	1.17^{fgh}	9.23^{g}	17.08^{b}
Farmer 3	140.33^{bc}	199.67^{de}	46.67^{a}	99.33^{d}	9.75	5.51^{cd}	8.44	19.33^{b}	42.33^{b}	10.15^{abc}	1.93^{bc}	0.89^{cd}	8.36^{f}	17.59^{g}
'Lleno de España'	150.67^{c}	182.00^{cde}	39.00^{a}	90.33^{cd}	11.62	5.77^{d}	10.18	19.86^{c}	42.51^{cd}	10.89^{cde}	2.60^{cd}	1.04^{ef}	7.02^{d}	17.71^{j}
WC	**118.76**	**159.28**	**39.41**	**78.83**	**5.04**	**5.53**	**4.45**	**20.73**	**43.40**	**10.96**	**2.14**	**0.88**	**6.49**	**17.50**
Pergamino	103.02^{a}	173.60^{bcde}	38.20^{a}	91.20^{cd}	6.21	4.60^{bc}	5.52	20.40^{e}	44.39^{g}	11.62^{ef}	1.82^{bc}	0.65^{b}	6.77^{cd}	18.17^{l}
Campana	126.00^{abc}	158.25^{abc}	46.50^{a}	76.75^{abcd}	4.53	9.04^{g}	3.89	21.96^{f}	46.54^{h}	11.31^{de}	1.17^{ab}	0.38^{a}	5.62^{ab}	17.00^{a}
Campi	108.04^{ab}	172.60^{bcde}	40.60^{a}	84.60^{bcd}	3.67	5.08^{cd}	3.27	21.52^{e}	42.40^{ef}	12.39^{fg}	2.00^{bc}	1.02^{de}	6.09^{bc}	17.92^{k}
Montevideo	132.00^{abc}	149.00^{abc}	38.60^{a}	70.40^{abc}	5.69	7.94^{ef}	4.85	19.39^{a}	40.48^{a}	10.68^{bcd}	3.00^{d}	1.24^{h}	7.38^{de}	17.21^{d}
Paysandú	111.08^{ab}	165.80^{abcd}	40.40^{a}	78.60^{abcd}	5.09	4.25^{b}	4.51	19.56^{a}	41.28^{a}	9.88^{ab}	2.70^{cd}	1.20^{gh}	7.39^{de}	17.46^{f}
Entre Ríos	132.60^{abc}	136.20^{ab}	33.60^{a}	71.00^{abc}	5.02	2.24^{a}	4.63	21.55^{e}	45.32^{fg}	9.89^{ab}	2.14^{cd}	0.76^{bc}	5.70^{ab}	17.25^{e}

CC cultivated cardoons, *WC* wild cardoons, *PH* plant height (cm), *PD* plant diameter (cm), *LW* leaf width (cm), *LL* leaf length (cm), *Y* total yield per hectare (Mg ha-1), *MC%* moisture content, *VS* volatile solid, *HC* hemicellulose, *Cel* cellulose, *Lig* lignin, *EE* ethereal extract, *N* nitrogen, *HHVdb* high heating value. Values followed by the same letter within the same column are not significantly different at $p<0.05$. In bold: mean values corresponding each to botanical varieties. *significant differences between botanical varieties ($p<0.05$). **harvest on October 2019 ***on dry matter basis (harvest on February 2020)

Table 3 Estimated yield of cultivated and wild cardoons according to the type of biofuel/bioenergy measured

Accession	Bioethanol ($l\ ha^{-1}$)	Biomethane Model 1		Biomethane Model 3		Direct combustion (MJ ha^{-1})
		$m^3\ kg^{-1}$ VS	$m^3\ ha^{-1}$	$m^3\ kg^{-1}$ VS	$m^3\ ha^{-1}$	
Cultivated cardoons	**3339.51**	**0.264**	**2521.58**	**0.188**	**1789.58**	**201,079**
'Lumbier'	3729.81	0.249	2666.76	0.171	1830.28	219,136
Farmer 1	3081.30	0.288	2610.71	0.207	1875.53	186,663
Farmer 2	4554.34	0.346	4314.02	0.281	3496.40	250,699
'Blanco Peralta'	2837.49	0.208	1822.43	0.122	1066.22	172,679
Farmer 3	2721.62	0.231	1952.01	0.156	1316.85	171,502
'Lleno de España'	3283.39	0.269	2739.30	0.196	1989.77	205,790
Wild cardoons	**1465.36**	**0.292**	**1300.45**	**0.221**	**984.00**	**88,200**
Pergamino	1821.83	0.281	1548.61	0.213	1177.54	112,836
Campana	1406.27	0.334	1299.53	0.269	1045.02	77,010
Campi	1065.68	0.291	952.34	0.225	734.02	65,766
Montevideo	1544.60	0.250	1213.71	0.175	850.88	97,925
Paysandú	1403.61	0.260	1174.17	0.183	823.25	88,871
Entre Ríos	1521.69	0.337	1559.31	0.262	1212.76	86,595

Values in bold indicate mean values for each botanical variety

4 Discussion

In order to obtain different kinds of biofuels from cardoon biomass, it is necessary to make a dual harvest at the plants senescent state. First, all the heads are collected for achenes extraction; after that, a second cut at ground level would allow to collect all remaining vegetative biomass (stalks and leaves). Achenes could be destined for oil extraction and biofuel production, while bioethanol, biogas (biomethane), or electrical/thermal energy (by direct combustion) could be obtained from the stems and leaves. An adequate equipment, with two cut levels, would made the harvest easy. One blade would cut the heads, while the second one would cut the rest of the biomass at ground level, simultaneously.

The amount of biomass produced and its chemical composition are the most important factors to be considered in order to determine its industrial use. The amount of biomass produced is directly related to the plant architecture (height and diameter) and the leaves number. As well as the most perennial biomass crops, the first year of culture is considered a crop stabilization period, and biomass yield is low [10]. In the second year, yield increases considerably and remains stable until the fifth or sixth cultivation year [9].

In concordance with previous studies [18, 20, 36], our results, obtained during the second year culture, reveal variability between and/or within botanical varieties for all biometric characteristics. In general, cultivated cardoon reached greater values than wild accessions for all traits related with the plant architecture and biomass production. Cultivated cardoons produced more than twice biomass than wild accessions, achieving values of 11.51 and 5.04 Mg ha^{-1}, respectively. Similar differences between cultivated and wild cardoons were observed by other authors [19, 36]. Nevertheless, some authors reported higher values than those found in this experiment. For example, Angelini et al. [9] reported plant heights close to 2 m in different cultivated cardoon accessions. In our study, only the accessions named Farmer 1 and Farmer 2 approached these values. Other authors [18, 37, 38] reported biomass yields ranging between 10 and 20 Mg ha^{-1} $year^{-1}$ for cultivated cardoon. In these studies, the biomass weight was estimated including the heads and achenes. Adding the weight of the achenes produced by cultivated and wild cardoons (1.32 and 1.40 Mg ha^{-1}, respectively, data recorded in a previous study [16]) to the dry canopy lignocellulosic biomass weight, the total biomass yield would reach values around 12.80 and 6.40 Mg ha^{-1} for cultivated and wild cardoon, respectively, reaching 'Lumbier' and Farmer 2 values for total biomass yield higher than 14.00 and 15.50 Mg ha^{-1}, respectively.

Of particular interest is to note that the cultivated accessions show, simultaneously, the highest and lowest values for biomass production. This fact demonstrates the wide range of genetic variability present in this group. Other authors [19, 21, 27, 36, 39] report always higher values for cultivated cardoons than wild cardoons; however, it is possible that the low number of accessions evaluated in these works and/or the low difference in their origins prevent detecting such variability. On the other hand, a wide variability between accessions (five cultivated and nine wild cardoons) was reported by Raccuia and Melilli [20]. Genetic variation detected between accessions can be used in genetic breeding programs.

The biomass moisture content negatively affects bioenergy production. There is a negative linear relationship between moisture content and calorific value [40]. In this trial, variation between accessions was observed for this trait, which is associated with the senescence status of plants at harvest time. The whole trial was harvested at the same time, so earlier accessions would have lower moisture content. The harvest time is, then, a crucial point to consider for the use of biomass as raw material for bioenergy production.

Lignocellulosic biomass is composed of cellulose and hemicellulose combined with lignin and other components, such as extractives, proteins, starch, and inorganic compounds to a lesser extent [10]. The type of biofuel to be obtained, the conversion processes to be applied, and the efficiency of these processes depend on the chemical characteristics of the biomass, especially of cellulose, hemicellulose, and lignin contents.

Chemical analysis of the cultivated and wild cardoon dry biomass reveals no differences between botanical varieties (except for ash content). However, significant differences between accessions were observed. Gominho et al. [41] also pointed out that the cardoon biomass chemical composition does not vary between botanical varieties, but it depends on the genotype. The contents of cellulose (40.48–47.93%), hemicellulose (18.90–22.73%), and lignin (9.63–12.62 %) found in our study are within the range of values that have been reported by other authors, 43.8–47.3%, 16.9–27.0%, and 6.9–16.1% for cellulose, hemicellulose, and lignin, respectively [42–47].

The potential amount of bioethanol to be generated is directly related to the cellulose and hemicellulose contents. Hemicellulose is mainly composed by xylan (> 90%). Shatalov and Pereira [33], through a hydrolysis selective process applied on cardoon biomass, determined that during the first-step dilute sulfuric acid hydrolysis, it is possible to achieve 86% of xylan conversion into xylose (5-carbon sugar). In the second-step enzymatic hydrolysis, 76% cellulose to glucose (6-carbon sugar) conversion is achieved. Then, xylose and glucose are the simple fermentable sugar inputs for bioethanol production.

The average amount of bioethanol per hectare feasible to be obtained from cultivated cardoon accessions was calculated to be more than twice over the average for wild cardoons. This difference is not only related to differences in cellulose and hemicellulose contents but also to the higher biomass production of cultivated cardoons, which also exceeds wild cardoon production by more than double. The accession Farmer 2 showed the highest potential bioethanol yield, which is associated both with its highest biomass yield and its highest cellulose and hemicellulose contents. Pesce et al. [48] reported bioethanol yield between 2143 and 3361 l ha^{-1} using biomass of the globe artichoke 'Spinoso sardo' grown in Sicily, Italy. This range of variation was due to different pretreatments. Jozami et al. [49] applied the same estimation methodology used in this study on *Spartina argentinensis* dry biomass and obtained values of bioethanol yield of about 1990 and 2535 l ha^{-1}, considering a hydrolysis efficiency of 60% and 90%, respectively. Sanderson et al. [50] reported that it is possible to obtain 330 l of ethanol from 1 Mg of switchgrass. Biomass yield for this last species is ranging between 5 and 11 Mg ha^{-1} [4], so that the ethanol yield per hectare would be in the order of 1650 and 3630 l. Estimated data indicate that the amount of bioethanol feasible to be obtained from one hectare of cardoon could be similar to that reported for other species proposed as raw material for second-generation bioethanol.

The lignin content is another determining factor for the biomass final use. Lignin negatively affects the biodegradability of lignocellulosic biomass since its anaerobic degradation is slow. Moreover, lignin would protect some holocellulose from degradation [34]. Several authors have reported negative effects of high lignin content on the enzymatic hydrolysis efficiency [51].

The feasibility of using cardoon as raw material for biomethane production has been studied previously. Oliveira et al. [52] analyzed only stems of a single cardoon variety whose chemical composition included 35% cellulose and 21% hemicellulose, indicating that this material is a good substrate for biogas and methane production with 53% CH_4 content. Pesce et al. [53] subjected samples of biomass (including stems, leaves, and heads) collected from cultivated and wild cardoons to an experimental anaerobic fermentation process without pretreatment nor additives addition. The experiment showed the biomethane yield ranged from ~200 to 245 m^3 per Mg of dry matter. Higher yields were obtained in cultivated cardoons due their greater biomass production and lower lignin content.

Our estimations of the potential biomethane production were performed taking into account Gunaseelan models 1 and 3 [34], both proposed to estimate the biomethane production from chemical constituent data of different types of biomass sources, from fruits and vegetable solid wastes (FVSW). Model 1 is based on a multiple regression where carbohydrates, lignin, lignin/ADF, nitrogen, and ash contents are dependent variables, while in model 3, predictor variables are carbohydrates, ADF, lignin/ADF, nitrogen, and ash contents. Model 3 predicts lower biomethane yield since it considers lignin, cellulose, nitrogen, and ash contents as negative factors.

According to our estimations, similar amounts of biomethane per kg of volatile solids could be obtained from cultivated and wild cardoons, although there is a slight tendency to be higher in the wild accessions. However, when yield per hectare is estimated, the cultivated accessions had twice as much as the wild ones due to their higher biomass yield. Despite having the highest value for lignin content, Farmer

2 widely exceeded all the other accessions in the amount of biomethane production estimated. This fact is correlated with the higher biomass production but could also be associated with the lower ash and nitrogen contents found in this accession. In this sense, if biomethane production is the final objective, Farmer 2 could be subjected to a breeding program in order to reduce its lignin content; thus, it could become an ideal raw material for this purpose.

Nitrogen content is another parameter that negatively influence the biodigestion process because proteins have very slow degradation rate [54, 55]. The N content in herbaceous biomass generally increases with the incorporation of nitrogen fertilizers into the soil [56]. *C. cardunculus* has the advantage of being a crop with low fertilization requirements so the N content would not be increased externally during cultivation. On the other hand, low ash content indicates high volatile solids content which is desirable for a biomass subjected to anaerobic digestion. Ashes are an inert material that only occupies volume in the biodigester, without any benefit; moreover, it can wear down the equipment and decrease the efficiency of the entire system [57]. Both nitrogen and ash content observed in the evaluated accessions are within acceptable ranges for a biomass subjected to an anaerobic digestion process [58].

The amount of biomethane per kg of volatile solid estimated for all the accession is similar to those values reported by Pesce [53] and are also similar or slightly lower than to those reported for rice straw (350 l kg^{-1} VS) [59], corn silage (312 l kg^{-1} VS) [59, 60], and organic waste rich in lignin (200 l kg^{-1} VS) [61].

High polysaccharide and low lignin content provide opportunities for biomethane obtaining through anaerobic digestion. On the other hand, high lignocellulose content promotes energy production by combustion. Biomass combustion plays an important role in energy production to obtain electricity or heating.

High heating value (HHV_{db}) is one of the most important characteristics of a fuel as it determines its energy content. It is defined as the amount of heat energy released during the complete combustion of unit mass of biomass. HHV_{db} between 17 and 18 MJ kg^{-1} were found for both cultivated and wild cardoons, in agreement with Foti et al. [62] and Fernández et al. [37] who reported HHV between 16 and 17 MJ kg^{-1} for dry cardoon biomass without the achenes. For Grammelis et al. [63] HHV without achenes is about 13.7 MJ kg^{-1} while, if achenes are included, this value adds up to 16.3 MJ kg^{-1}. The HHV of a lignocellulosic material is positive and highly correlated with the lignin content, while ash and moisture contents negatively affect the HHV [64]. In our essay, Pergamino was the only accession that surpassed 18 MJ kg^{-1} and showed one of the highest values for lignin content (3/12 in the ranking), one of the lowest moisture content (9/12 in the ranking), and intermediate values for ash content, demonstrating that the three-factor combination is relevant for determining the biomass HHV.

The high inorganic element concentration in herbaceous biomass feedstock causes difficulties in direct combustion systems such as fouling of boilers. According to several authors, *C. cardunculus* biomass is characterized by high ash content compared to other herbaceous plants used as raw material for bioenergy such as *Miscanthus* (2–3%), switchgrass (3–6%), or giant reed (4–7%) [65]. These last authors reported values between 8 and 14% for ash content in cardoon biomass which is in agreement with values previously reported for cultivated and wild cardoons (14%) [61]. On the other hand, for Mantineo et al. [66], this value was 7.4%, which is similar to those obtained in this study (6.49 and 7.48% for wild and cultivated cardoons, respectively), being ash content the only one chemical variable for which significant differences between botanical varieties were observed. The ash content depends on the edaphic-climatic conditions, harvesting techniques, and the fraction of the plant collected. Coulson and Bridgwater [67] found values of 4.8, 11.2, and 15.08% for *C. cardunculus* stems, leaves, and heads, respectively, whereas Gominho et al. [41] reported values between 5.4 and 10.0% for stems and between 15.1 and 29.6% for leaves. Total ash concentrations in forages usually decrease as forages mature [68]. Thus, harvesting biomass at late maturity stages, besides reducing the moisture content, it would also minimize the concentrations of inorganic elements. In our experiment, biomass was cut manually, avoiding contamination with soil particles. In addition, cutting the vegetative biomass was made at the end of the productive cycle, and after heads were harvested, so only the remaining stems and leaves were considered.

Although, on average, cultivated cardoon accessions showed higher ash content than wild accessions, once again, Farmer 2 stands out, having the lowest ash contents with an HHV_{db} higher than all accessions average. These characteristics, together with a high lignin content, make Farmer 2 the accession with the highest potential for energy efficiency through direct combustion.

5 Conclusions

Biomass yield and chemical characteristics make cardoon a promising candidate to be grown for energy purposes under very low crop inputs in the edapho-climatic conditions prevailing in central Argentina or other regions of the world with comparable edapho-climatic conditions. Although no differences were observed between botanical varieties for the biomass chemical composition, the higher yield of cultivated cardoons give to this botanical variety a greater energy potential.

The different uses proposed for lignocellulosic biomass are alternative to each other. Varieties with specific characteristics could be developed to be used as raw material for bioethanol or biomethane production or thermal energy generation by direct combustion.

The local variety Farmer 2 stands out among all cultivated cardoon accessions because it showed the highest yield and qualitative characteristics suitable for different kinds of bioenergy production, such as high cellulose and hemicellulose content, low ethereal extracts and ash contents, and heating values higher than all accessions average. Although this accession had a higher moisture content than some other accessions, it is acceptable and could be further reduced delaying the biomass harvest for a few days in order to increase tissue senescence. This practice also would increase the heating value.

Author contribution All authors contributed to the study conception and design, material preparation, data collection, and analysis. The first draft of the manuscript was written by Micaela Mancini and Ana Breso, and all authors commented on the previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval Not applicable

Competing interests The authors declare no competing interests.

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